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NOVEL PRECURSORS FOR ORGANOMETALLIC VAPOR PHASE EPITAXY

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ABSTRACT

During the development of organometallic vapor phase epitaxy (OMVPE) for the growth of III/V semiconductor materials, the choice of group III and group V source molecules has been limited: 1) only trimethyl- and triethyl- group III and antimony compounds, developed for other applications, were available; 2) the hydrides were the only As and P sources capable of producing device quality material. The hazard posed by the hydride sources, due to their extreme toxicity as well as their storage in high pressure cylinders, was a major motivation for the development of new precursor molecules. This led to the realization that many features of the OMVPE process could be improved by the development of "designer" source molecules. This paper will emphasize the tertiarybutyl- As, P, and Sb precursors $C_4H_9AsH_2$, $C_4H_9PH_2$, and $C_4H_9Sb(CH_3)_2$. However, recent results using alternate In precursors, such as triisopropylindium $(C_3H_7)_3In$, will be included. The fundamental aspects of the design of source molecules, including pyrolysis routes, will be mentioned; however, the focus is on the practical results obtained using these precursors for the OMVPE growth of III/V semiconductors.

1. Introduction

Organometallic vapor phase epitaxy (OMVPE) has gradually evolved into the leading technique for the production of III/V semiconductors and the elegant and elaborate structures required for the highest performance electronic and photonic devices. However, some improvements in the technique are still required, such as reductions in carbon contamination, growth temperature, and hazard. Substantial improvements in each of these areas can be achieved by the use of improved precursor molecules. Until recently choosing a precursor was largely an empirical exercise of trying the various chemicals selected from suppliers' catalogues to see which gave the best semiconductor layers. The precursors were generally of the type MR_n where M represents the group III or V element of interest and R was largely limited to methyl or ethyl radicals or H radicals for the group V precursors. Only during the last few years have the serious limitations imposed on OMVPE results by this restricted choice of source molecules begun to be understood. This has led to the development of new precursors and to the important realization that design of the precursor molecules is an essential part of the design of the overall epitaxial process. We are now entering the era of "designer" molecules where specific and distinct precursor molecules will be developed having the optimum characteristics for each of the various vapor growth processes using

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organometallic molecules: OMVPE, chemical beam epitaxy (CBE), atomic layer epitaxy (ALE), laser assisted OMVPE, and others. This paper gives an overview of some of the newer group III and group V precursors.

2. Requirements

The first requirement of a precursor is that it be sufficiently volatile to allow acceptable epitaxial growth rates. This normally requires room temperature vapor pressures of ˜1 Torr for the relatively nonvolatile group III and Sb precursors and at least an order of magnitude higher for the As and P precursors. Tables I and II give the vapor pressures for several group III and group V precursors, respectively.

The major factor driving the search for improved group V precursor molecules has been the demand for less hazardous precursors. Arsine and phosphine are very dangerous because of their extreme toxicity combined with their high vapor pressures of many atmospheres. Liquid, organometallic sources are approximately 100X less hazardous due to their lower vapor pressures, resulting in slower dispersal into the atmosphere, leading to lower concentrations[1]. Fortunately, many group V organometallic molecules are considerably less toxic than the hydrides. The outstanding example is *tertiarybutyl* phosphine (TBP), with a toxicity orders of magnitude lower than that for phosphine. Available toxicity data for the group V precursors are included in Table II.

A third requirement is that the precursor molecule pyrolyze at sufficiently low temperatures to allow growth at the substrate temperatures desired. The pyrolysis temperature is generally directly related to the M-R (metal-radical) bond strength, but may also be related to the pyrolysis mechanism. The M-R bond strength decreases with an increase in the number of carbons bonded to the central carbon, i.e., the one forming a bond to the M atom. Thus, the temperature at which homolytic fission of the M-R bond occurs decreases in the order M-methyl, M-ethyl, M-*iso*-propyl, M-*tertiary*-butyl, etc.[1].

A fourth requirement is that the precursor be useful for producing high purity epitaxial layers. This requirement involves two factors. First, the molecules must be sufficiently stable to allow purification by fractional distillation and related techniques. Perhaps more important is the intrinsic carbon contamination resulting from the precursors. To avoid incorporation of large quantities of carbon into the epitaxial layers requires either a supply of H radicals to convert the alkyl groups to stable alkane molecules, such as methane, ethane, etc. or the elimination of carbon by the use of relatively stable organic radicals. Methyl radicals are quite reactive, so frequently lead to carbon incorporation into the growing solid, especially for Al-containing materials[2]. More stable radicals, such as C_2H_5 and *t*-C_4H_9, apparently result in very little carbon contamination[3].

The above discussion of pyrolysis temperature and carbon contamination is somewhat naive, since it implicitly assumes that pyrolysis occurs by homolysis (or heterolysis), i.e., by the sequential elimination of radicals from the parent molecule until the element is incorporated into the solid. For this process, the strength of the first bond determines the pyrolysis temperature and the nature of the resulting radicals largely determines the rate of carbon incorporation into the growing solid. However, the pyrolysis processes may be considerably more complex, as discussed in Section 4. Here we will simply note that other pyrolysis processes may occur more rapidly than homolysis and produce no reactive radicals. β-elimination reactions[1] occur without radical production, so are favorable for

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avoiding carbon incorporation, but do not occur for methyl radicals. Pyrolysis of TMAs is believed to occur via hydrogenolysis[4], as discussed below. The rate of this process is not determined by the As-CH$_3$ bond strength and no CH$_3$ radicals are produced.

The fifth requirement is that the precursors not participate in deleterious parasitic gas phase reactions that deplete the nutrient from the vapor. For example, the triethyl-group III precursors react with arsine and phosphine to form adducts. These decompose on the warm reactor walls resulting in the formation of a low vapor pressure polymeric condensed phase. This lowers the growth efficiency, increasing the usage of expensive precursors. Such uncontrolled reactions also give nonuniformities in growth rate and solid composition for III/V alloys.

The design of effective precursor molecules requires an understanding of both the general characteristics of organometallic molecules and the pyrolysis processes for specific precursor molecules. This paper gives a brief overview of the search for improved precursor molecules. This involves empirical results obtained for OMVPE growth of III/V compounds using various precursors as well as the results of experiments designed to reveal the pyrolysis processes and growth mechanisms.

3. Group III Precursors

The typical group III precursors for OMVPE growth of III/V semiconductors are the trimethyl compounds of Al, Ga, and In. These materials are readily available in high purity form and have vapor pressures convenient for atmospheric pressure growth. A disadvantage is the relatively high reactivity of CH$_3$ radicals produced. This results in both fairly high pyrolysis temperatures and carbon contamination of the epitaxial layers under some conditions, particularly for Al-containing materials and for CBE growth.

To minimize carbon contamination, the triethyl group III alkyls are sometimes used. The highest purity GaAs produced to date by OMVPE was grown using triethylgallium (TEGa) and either arsine[5] or *tertiarybutyl* arsine (TBAs)[6]. The triethyl alkyls have two advantages: 1) Homolysis produces ethyl radicals, which are much more stable than methyl radicals. 2)β-elimination reactions, that produce C$_2$H$_4$ molecules and leave an H radical attached to the metal[1], are expected to be important for the ethyl radicals, as well as for the *iso*-propyl and *t*-butyl radicals. The triethyl group III alkyls are, however, less convenient precursor molecules for OMVPE than the trimethyl alkyls since they have much lower vapor pressures and are also much less stable. Triethylindium (TEIn) is known to decompose in the bottle. In atmospheric pressure OMVPE reactors the triethyl-III precursors participate in parasitic reactions. The lack of stability makes the triethyl group III precursors more useful for both low pressure and low temperature growth.

There is clearly a need for the development of novel group III precursors for OMVPE which combine the best characteristics of the trimethyl and triethyl alkyls. An apparently promising In precursor is ethyldimethylindium (EDMIn). Whereas TMIn is a solid, with a vaporization rate which is found to vary with time, EDMIn is a liquid which yields InP of purity similar to that obtained using TMIn[7,8]. However, alkyl exchange reactions are expected to result in several combinations of methyl and ethyl radicals on the molecules evaporated from the liquid. This might lead to an instability in vapor pressure and other characteristics, although such behavior has not been verified.

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A very recently developed liquid In precursor is triisopropylindium ($(C_3H_7)_3In$, TIPIn). It pyrolyzes at relatively low temperatures, with a T_{50} of approximately 110°C, 200°C lower than for TMIn[9]. The pyrolysis process is apparently simple homolysis, producing mainly C_6H_{14}. Unfortunately, it has a vapor pressure of only 0.32 Torr at room temperature[9]. This problem is shared by a number of other alternate In precursors[10]. It also appears to participate in prereactions that lower the growth efficiency. Nevertheless, it has been used, with arsine, for the growth of InAs with good surface morphologies at temperatures as low as 300°C (with a V/III ratio of 460). Preliminary indications are that the carbon contamination is an order of magnitude less than observed using either TMIn or EDMIn with arsine[9].

New group III precursors are currently being developed that offer considerable promise for reduced carbon contamination in AlGaAs grown by OMVPE. Adduct compounds of the type AlH_3-$N(CH_3)_3$ [11] are expected to pyrolyze without the production of free methyl radicals, and have, in fact, been used to produce materials with low carbon concentrations. The vapor pressures of such adduct molecules are typically below the values desired for OMVPE. However, this should present essentially no problem for UHV techniques such as CBE. Naturally, the group III hydrides would be excellent precursors, except for their instability. Formation of the adduct between alane and trimethylamine produces a marginally stable precursor. Unfortunately, it is a solid at room temperature. However, the similar AlH_3-$N(C_2H_5)_3$ is a liquid[12]. The related gallane compounds are even less stable than the alane compounds. Thus, they may be suitable only for CBE growth[13].

4. Group V Precursors

AsH_3 and PH_3 are attractive precursors since they provide H radicals on the surface leading to the removal of C-containing radicals from pyrolysis of the group III precursors. The hydrides are also readily available with relatively high purity levels.The main disadvantage is the extreme hazard associated with their use. Arsine and phosphine are at the upper end of the acceptable range of stability. This leads to incomplete pyrolysis at normal growth temperatures, especially for PH_3. Interestingly, stibine (SbH_3) is so unstable that it decomposes during storage at room temperature. The metal-methyl bond is generally weaker than the metal-hydrogen bond. However, TMSb is more stable in the sense that it pyrolyzes at higher temperatures than the corresponding hydride. TMSb is the standard antimony source for OMVPE.

As mentioned above, the M-R bond strength is decreased as the number of carbons bonded to the central carbon atom increases. Thus, precursors with M-ethyl, M-*n* -propyl, M-*n*-butyl, and M-*iso* -butyl bonds pyrolyze at similar temperatures that are somewhat lower than for M-H and M-methyl bonds. This is illustrated by the plot of percent pyrolysis versus temperature in Fig. 1. The data were obtained for the various precursors in the same isothermal, flow-tube apparatus with a residence time of several seconds. Even weaker are the M-*t*-butyl bonds. Normally, the weakest bond in a molecule is the first to break. Thus, the pyrolysis temperature for TBAs, with one As-*t*-butyl bond and 2 As-H bonds, is low due to the weak As-*t* -butyl bond strength.
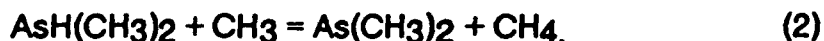
The requirement for high purity semiconductor layers imposes the constraint that the molecule contain at least one M-H bond, particularly when trimethyl- group

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III alkyls are used. Empirically, two or more M-H bonds are better. However, as we examine specific precursor molecules, it will be seen that this rule is overly simple. A disadvantage of increasing the number of M-H bonds is the empirically observed increase in the toxicity of the group V precursors[14], as seen in Table II.

The vapor pressures for TMAs and DMAs are attractive, although the pyrolysis temperatures are somewhat higher than desired. A severe disadvantage of TMAs for OMVPE of GaAs is the high level of carbon contamination observed. Li et al[4] studied the pyrolysis of TMAs in a flow-tube reactor. The percent pyrolyzed is plotted versus temperature in Figure 1 for a D_2 ambient. In He the decomposition temperature is increased. Pyrolysis in He is thought to occur via a sequence of methyl radical elimination steps[15]. The ambient effect often indicates the involvement of radicals in the growth process. This was tested by observing the effect of the addition of toluene, a methyl radical scavenger, to the system. No effect was seen in a D_2 ambient. Thus, the ambient effect was interpreted in terms of a hydrogenolysis mechanism:

$$As(CH_3)_3 + D_2 = AsD(CH_3)_2 + CH_3D. \qquad (1)$$

The products are indeed CH_3D and $AsD(CH_3)_2$ in D_2 and CH_4 and $AsH(CH_3)_2$ in H_2, as expected from this model. This hydrogenolysis process, which leads to a sequential replacement of methyl radicals by H in an H_2 ambient, would lead to a reduced level of carbon contamination if allowed to go to completion in the gas phase above the substrate. Unfortunately, this does not occur, partly because the DMAsH formed by reaction (1) pyrolyzes by homolysis, producing a CH_3 radical which subsequently attacks the parent molecule, abstracting the H[15]

$$AsH(CH_3)_2 + CH_3 = As(CH_3)_2 + CH_4. \qquad (2)$$

This reaction may be responsible for the high levels of carbon found in GaAs grown using DMAs and TMGa[15]. This example illustrates why a knowledge of pyrolysis kinetics is an important factor in the design and evaluation of new precursor molecules.

The methyl-phosphorus precursors are too stable to be useful for OMVPE. TMSb is the most widely used methyl-Sb precursor; however, the pyrolysis temperature is somewhat higher than optimum for growth of the small band gap materials. An additional problem is that the use of TMSb in conjunction with TMGa and TMAl results in AlGaSb with extremely high levels of carbon contamination[16]. The pyrolysis of TMSb in He is due to sequential methyl elimination reactions. In D_2 (or H_2) the pyrolysis rate is dramatically increased. The resulting value of T_{50} is given in Table II. The effects of added radical scavengers as well as methyl radical sources indicate that the pyrolysis reaction in H_2 is due to the following sequence: 1) homolysis to produce methyl radicals; 2) reaction between methyl radicals and the ambient producing H radicals; 3) attack of the parent molecule by the H radicals[17].

All three ethyl-arsenic precursors, TEAs, diethylarsine (DEAs), and monoethylarsine (EAs), have been used for the OMVPE growth of GaAs. TEAs gives unacceptable carbon contamination levels of $>10^{18}$ cm^{-3}[18]. By far the best purity levels are obtained using EAs, with 77-K mobilities as high as 55,300 cm^2/Vs[19]. Speckman and Wendt[18,19] as well as Li et al[20] reported the pyrolysis reactions to involve radical cleavage for all three precursors. The lack of a

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β-hydrogen elimination route for TEAs, which would produce DEAs and EAs, may explain the high levels of carbon obtained. The pyrolysis of ethylarsine produces highly reactive AsH_2 radicals on the surface, perhaps explaining the low carbon doping levels observed.

The organometallic group V precursor giving the best results is *tertiary-butylarsine*. 77-K mobilities of 160,000 cm^2/Vs have been reported using TEGa and TBAs[6]. Using TMGa, which gives more carbon contamination from CH_3 radicals, p-type materials are obtained with either TBAs or arsine. The results of detailed studies of carbon contamination levels indicate that TBAs gives somewhat less carbon than arsine[21]. This is consistent with the lower temperature pyrolysis of TBAs giving AsH and/or AsH_2 radicals, as discussed below.

Early studies of TBAs pyrolysis indicate the mechanism to be two parallel unimolecular reactions, yielding AsH and AsH_3 [22]. More recent results suggest that radical processes may play a role in TBAs pyrolysis[23], as discussed below for TBP. The vapor pressure of TBAs is favorable for OMVPE and pyrolysis occurs at temperatures several hundred degrees below those for AsH_3, as seen in Fig. 1.

The only successful organometallic phosphorus OMVPE precursor is TBP. Recent studies have yielded InP grown using TMIn with 77-K electron mobilities of 130,000 cm^2/Vs[24]. The pyrolysis of TBP has been studied extensively,[25] including the addition of *t*-butyl radicals to the system as well as the use of deuterated TBP-d_2[26]. As expected, the pyrolysis of TBP occurs at much lower temperatures than for PH_3. The pyrolysis reactions are seen to be complex, since the input partial pressure affects both the pyrolysis rate and the reaction products[26]. At low input partial pressures, the major product is isobutene (C_4H_8). At higher input partial pressures, the pyrolysis occurs at lower temperatures and the major product is isobutane (C_4H_{10}). This can only be explained if pyrolysis occurs by competing unimolecular and bimolecular processes. In general, unimolecular processes dominate at low partial pressures, while bimolecular processes may dominate at higher partial pressures. The experimental data indicate that C_4H_8 is formed by a unimolecular process, i.e., by decomposition of C_4H_9, produced by a homolysis reaction, to form C_4H_8 + H, while C_4H_{10} is formed by a competing bimolecular route. When the H radicals attached directly to the P atom are replaced by D to form TBP-d_2, the product is C_4H_9D[26], which indicates that the *t*-butyl radical interacts with the D attached to the P, via the bimolecular reaction,

$$C_4H_9 + (C_4H_9)PD_2 = C_4H_9D + (C_4H_9) PD. \qquad (3)$$

This hypothesis was tested by examining the effect of the addition of *t*-butyl radicals on the TBP pyrolysis rate. The *t*-butyl radicals were generated from azo-*t*-butane (ATB), which pyrolyzes at 250 C to produce the desired radicals plus inert N_2. The results convincingly demonstrate the attack of *t*-butyl radicals on the parent molecule, reaction (3). A similar effect is observed for TBAs. In addition, the pyrolysis of TBAs was demonstrated to cause the pyrolysis of TBP, indicating that *t*-butyl radicals are produced during the pyrolysis of TBAs[23]. Thus, a reaction similar to Eqn. (3) appears to occur for TBAs.

Very recently, several Sb precursors have been developed to replace TMSb and TESb. A useful precursor is triisopropylantimony (TIPSb). It pyrolyzes[27], by a combination of homolysis and β-elimination reactions, at temperatures

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approximately 100°C lower than for TMSb, as seen in Table II. TIPSb has been used with TMIn and TMGa for the OMVPE growth of high quality layers of both InSb and GaSb[28]. Perhaps even more useful is tertiarybutyldimethylantimony (TBDMSb). The pyrolysis, at temperatures well below those required for TMSb, occurs by homolysis, producing t-butyl radicals and dimethylantimony. The data suggest that pyrolysis proceeds by disproportionation reactions[29], without the production of methyl radicals. This is encouraging for avoiding carbon contamination of the epitaxial layers. High quality epitaxial InSb layers have been grown at temperatures as low as 325C, even lower than for TIPSb, using TMIn and TBDMSb[30].

5. Summary

The use of various group III and group V precursors for OMVPE has been described in terms of: 1) the characterization of the precursor molecules, themselves; 2) the pyrolysis reactions at atmospheric pressure; and 3) the growth results including the properties of the epitaxial layers with emphasis on carbon contamination. This allows a rational approach to the design of precursors for OMVPE.

TMGa and TMIn can be used with acceptable carbon contamination levels when the group V precursors are the hydrides, or molecules of the type MRH_2. This apparently provides atomic H to react with the CH_3 radicals produced by pyrolysis of the trimethyl-III precursors. The use of TEGa gives lower carbon doping levels, but at the price of increased parasitic reactions.

The use of TMAl (with TMGa and arsine) invariably results in AlGaAs layers with carbon contamination levels of 10^{16} to 10^{17} cm^{-3}. This has led to the successful development of a new family of precursors, including trimethylaminealane. When used with TEGa and arsine, TMAA results in AlGaAs layers with substantially reduced levels of carbon contamination.

The optimum replacement for phosphine is clearly TBP. It is a liquid having a favorable vapor pressure and a toxicity level much below that for PH_3. It yields high quality InP layers. The analogous arsenic compound, TBAs, is the leading replacement for arsine. The carbon contamination levels of GaAs grown using TMGa and TBAs are actually lower than for arsine using the same growth conditions. Another precursor having a favorable vapor pressure and 2 hydrogen ligands attached directly to the As is EAs. It must still be considered as a viable candidate.

Several novel antimony precursors, including TIPSb and TBDMSb, have been developed to replace TMSb for low temperature OMVPE growth and to reduce carbon contamination levels. Both have been used to grow high quality layers of GaSb and InSb.

We have clearly entered a new era where design of the precursor molecules will be considered an integral part of the overall process design. It is likely that specific molecules will be designed for each of the variations of OMVPE, such as CBE, ALE, selective epitaxy, etc.

ACKNOWLEDGMENTS

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Table I. Characteristics of Several Group III Precursors for Epitaxial Growth. (Vapor pressure (V.P.) numbers from Ref. [1] except where noted.)

Precursor	Vapor Pressure/ Temperature (Torr/C)	Advantages	Problems
TMAl	9/20	V. P. Stability	Carbon
TEAl	0.5/55	Carbon	V. P. Stability
TMAA	1.8/50[a]	Low Carbon	V.P. Stability(?)
TMGa	178/20	V. P. Stability	Carbon
TEGa	3.4/20	Carbon	V. P. Stability
TMIn	1.7/20	V. P.	Solid Drift of "V. P."
TEIn	1.2/40		V. P. Stability
EDMIn	0.85/17[c]	V.P. Liquid	Homogeneity
TIPIn	0.32/25[d]	Low Carbon Low Temperatures	V.P. Stability

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[b] N.I. Buchan, T.F. Kuech, M.A. Tischler, and R. Potemski, J. Crystal Growth 107, 331 (1991).
[c] Ref [7].
[d]C.H. Chen, C.T. Chiu, G.B. Stringfellow, and R.W. Gedridge, J. Crystal Growth (to be published).

Table II: Properties of several group V sources for epitaxy. Vapor pressure and toxicity is from ref. 1, unless indicated. Pyrolysis temperatures (T_{50}) are from experiments in a flow-tube reactor with a residence time of a few seconds.

Precursor	Vapor Pressure p.Torr/T.°C	T_{50}(°C)	Toxicity LC_{50}** (TLV*)	Carbon Doping TMGa/TMIn
PH_3		850	11-50 (0.3)	Very Low
TBP	141/10	450	>1100	Low
AsH_3		600	5-50 (0.05)	Very Low
TMAs	238/20	530	20,000	Very High
TEAs	5/20	490	500-1000***	High
DMAs	176/0	460	130	High
DEAs	40/20	440	300	Low
EAs	400/20	440		Low
TBAs	96/10	380	70	Very Low
$PhAsH_2$ (C_6H_5)AsH_2	1.8/20[a]	———		High
TMSb	82/20	450		High
TESb	4/25	———		
TIPSb (C_3H_7)$_3$Sb	0.7/30[c]	300		
TBDMSb (C_4H_9)(CH_3)$_2$Sb	7.3/23[d]	300		

* TLV based on eight hour day; ** From rat mortality study, 4 hour exposure; ***Oral dose in mg of material per kg of animal weight.

a Ref [24]

b Ref [28]

c Ref [27].

d. Ref [29].

FIGURE CAPTIONS

Figure 1. Percent pyrolysis in a D_2 ambient versus temperature for several As precursors. All measurements were made in the same ersatz reactor under nominally the same conditions.

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